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ORIGINAL ARTICLE

Convenient on water synthesis of novel derivatives of dicoumarol as functional vitamin K depleter by Fe_3O_4 magnetic nanoparticles

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KEYWORDS

Fe_3O_4 nanoparticles;
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Abstract The Fe_3O_4 nanoparticles were successfully prepared and characterized by X-ray diffraction (XRD), Fourier transform-infrared (FT-IR), and transmission electron microscopy (TEM). The magnetic property of the prepared nanoparticles was investigated by magnetization analysis and the measured magnetization of NPs was found to be considerably lower than the values measured from bulk magnetite. The catalytic efficiency of the prepared nanoparticles was subsequently investigated as a magnetically recyclable and safe catalyst for the green synthesis of new dicoumarols via the one-pot condensation of 4-hydroxycoumarin with aryl glyoxals on water. Catalyst loadings can be as low as 2 mol% to give good yields of the corresponding products. This present method has many advantages, such as the high product yield, avoidance of toxic organic solvents, and simple work-up procedure.

1. Introduction

Dicoumarol, a derivative of coumarin, is a naturally occurring anticoagulant that functions like warfarin as a vitamin K antagonist. Dicoumarols are the bridge substituted dimers of 4-hydroxycoumarin which have been employed for the prevention and treatment of thrombosis. They are also used in biochemical experiments as inhibitor of reductases (Link, 1941). According to the importance of some compounds containing coumarin nucleus in pharmaceutical research, the chemistry of this class of compounds has recently attracted the attention of chemists (Barzegar et al., 2011; Karami et al., 2012a, 2013a; Litinas et al., 2011). Although dicoumarol was firstly discovered in mouldy wet sweet-clover hay, several methods have been described in the literature to synthesize its derivatives such as, total synthesis of dicoumarols starting from salicylaldehyde and formaldehyde (Cherkupally and Mekala, 2008), biosynthesis of dicoumarol employing

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micro-organisms such as *Penicillium jenseni* (Bellis et al., 1967), and Knoevenagel condensation of 4-hydroxycoumarins with carbonyls using several catalysts (Hamdi et al., 2008; Kolos et al., 2007; Siddiqui and Farooq, 2011; Ziarani and Hajiabbasi, 2013).

To develop environmentally benign reaction conditions and media for organic transformations with excellent efficiency and selectivity, water has been shown to be a useful solvent or media (Karami et al., 2012b). Recently, organic synthesis on water was reviewed by Fokin and co-workers (Chanda and Fokin, 2009). Magnetically recyclable nanocatalyst systems for the organic reactions have also attracted considerable attention. In this context, we report the use of Iron oxide nanoparticles (Fe_3O_4 NPs) as an eco-friendly and efficient catalyst for the synthesis of some new and known dicoumarols containing an aryloyl group. Fe_3O_4 NPs were extensively applied as a powerful catalyst for organic transformations (Karami et al., 2012c,d). Moreover, the composite containing Fe_2O_3 and Fe_3O_4 NPs (Ahmad, 2013) have been used for the cellular separation (Roveimiab et al., 2012), bioadsorbents of biotin (Fartani et al., 2007), and potential solid support for recyclable biocatalysts (Rahman et al., 2013).

2. Experimental

All chemicals were purchased from Merck and Aldrich. Aryl gloxals were synthesized in accord with our previous method (Karami et al., 2011). The reactions were monitored by thin layer chromatography (TLC; silica-gel 60 F_{254}, *n*-hexane: ethyl acetate). IR spectra were recorded on a FT-IR JASCO-680 and the ^{1}H NMR spectra were obtained on a Bruker-Instrument DPX-400 and 300 MHz Avance 2 model. The varioEl CHNS Isfahan Industrial University was used for elemental analysis. The powder X-ray diffraction (XRD) pattern was obtained by a Bruker AXS (D8, Avance) instrument employing the reflection Bragg–Brentano geometry with CuKα radiation. Transmission electron microscopy (TEM) images were taken with a Philips CM-10 TEM microscope operated at 100 kV. The structures and purity of the obtained products were deduced from their IR, elemental analysis, and NMR spectral data.

2.1. Preparation of Fe_3O_4 NPs

$FeCl_3{\cdot}6H_2O$ (6.1 g, 0.02 mol) and $FeCl_2{\cdot}4H_2O$ (2.35 g, 0.01 mol) were dissolved in 100 mL de-ionized H_2O under magnetic stirring for 10 min, then, the solution was heated to 90 °C under nitrogen atmosphere. Subsequently, the ammonium hydroxide solution (10 mL, 25%) was added drop by drop to the reaction mixture and was allowed to continue for about 1 h. The reaction mixture was cooled to room temperature and black precipitate separated in a magnetic field from the reaction mixture, repeatedly washed with de-ionized H_2O for several times to remove the impurities.

2.2. Preparation of dicoumarols **3**

A mixture of 4-hydroxycoumarin **1** (2 mmol), aryl glyoxals **2** (1 mmol) and Fe_3O_4 NPs (2 mol%) in H_2O (10 mL) was heated at 80 °C for an appropriate time. The progress of the reaction was monitored by TLC. Upon completion, the mixture was poured on ice. After formation of precipitate, the solid was filtered off, dried and dissolved in a hot mixture of EtOH/THF (2:1). Fe_3O_4 NPs were separated by a magnet and pure product obtained by recrystallization from solvent. In some cases, column chromatography is needed.

2.3. Spectral data of new compounds

4-Flouro-benzoyl[bis(4-hydroxycoumarin-3-yl)]methane (***3b***): M.p. 235–237 °C; IR (KBr) $\tilde{\nu}$ = 3500–3300, 3066.26, 2887, 1695, 1650, 1619, 1600, 1567, 1271, 1225, 1107 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.15 (s, 2H), 7.89 (dd, 2H, J_1 = 8.2, J_2 = 1.6 Hz), 7.79–7.75 (m, 2H), 7.56–7.50 (m, 2H), 7.33–7.24 (m, 4H), 6.94 (t, 2H, J = 8.6 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 192.91, 165.40, 152.41, 133.27, 132.00, 130.77, 130.65, 125.08, 124.56, 116.75, 116.35, 115.97, 115.68, 42.80.

4-Methoxy-benzoyl[bis(4-hydroxycoumarin-3-yl)]methane (***3e***): M.p. 265–267 °C; IR (KBr) $\tilde{V}$ = 3500–3300, 3076, 2978, 1684, 1650, 1620, 1601, 1571, 1263 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.22 (s, 2H), 8.00 (dd, 2H, J = 8.2, 1.6 Hz), 7.77–7.72 (m, 2H), 7.55–7.49 (m, 2H), 7.32–7.24 (m, 4H), 6.77–6.72 (m, 2H), 6.00 (s, 1H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.13, 165.22, 163.55, 152.40, 133.08, 130.48, 128.30, 124.94, 124.57, 116.68, 116.48, 113.88, 55.46, 42.62.

3-Methoxy-benzoyl[bis(4-hydroxycoumarin-3-yl)]methane (***3f***): M.p. 205–207 °C; IR (KBr) $\tilde{V}$ = 3500–3300, 1693, 1655, 1619, 1602, 1567, 1273, 1427 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.16 (s, 1H), 8.00 (dd, 2H, J = 8.2, 1.6 Hz), 7.55–7.49 (m, 2H), 7.34–7.24 (m, 6H), 7.12 (t, 1H, J = 8.2 Hz), 6.94–6.90 (m, 1H), 6.00 (s, 1H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.21, 165.28, 159.72, 152.40, 136.93, 133.17, 129.42, 125.03, 124.52, 120.26, 120.15, 116.73, 116.42, 112.46, 42.91.

4-Chloro-benzoyl[bis(4-hydroxycoumarin-3-yl)]methane (***3g***): M.p. 250–252 °C; IR (KBr) $\tilde{V}$ = 3500–3300, 3080, 2884, 1713, 1665, 1650, 1614, 1564, 1266, 1090, 767 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 11.10 (s, 2H), 7.85 (d, 2H, J = 6.0 Hz), 7.72 (d, 2H, J = 5.2 Hz), 7.62–7.52 (m, 4H), 7.31–7.25 (m, 4H), 6.28 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 196.16, 165.92, 163.33, 152.27, 135.90, 131.66, 131.24, 129.32, 125.94, 123.83, 123.45, 118.09, 115.87, 101.64, 42.92.

2-Naphthoyl[bis(4-hydroxycoumarin-3-yl)]methane (***3h***): M.p. 255–257 °C; IR (KBr) $\tilde{V}$ = 3550–3300, 1694, 1653, 1617, 1565, 1454, 1280 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.24 (s, 2H), 8.27 (s, 1H), 8.01 (dd, 2H, J_1 = 8.2, J_2 = 1.6 Hz), 7.83–7.72 (m, 4H), 7.54–7.43 (m, 4H), 7.33–7.23 (m, 4H), 6.19 (s, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 177.38, 166.60, 163.65, 152.32, 134.48, 134.38, 131.82, 131.50, 129.13, 127.95, 127.54, 126.70, 124.15, 123.90, 123.33, 118.50, 115.78, 101.67, 43.14.

3. Results and discussion

The Fe_3O_4 NPs, homogeneous in size and composition, were prepared according to previous methods (Liu et al., 2008) by modification and characterized by X-ray diffraction (XRD), Fourier transform-infrared (FT-IR), and transmission electron microscopy (TEM).

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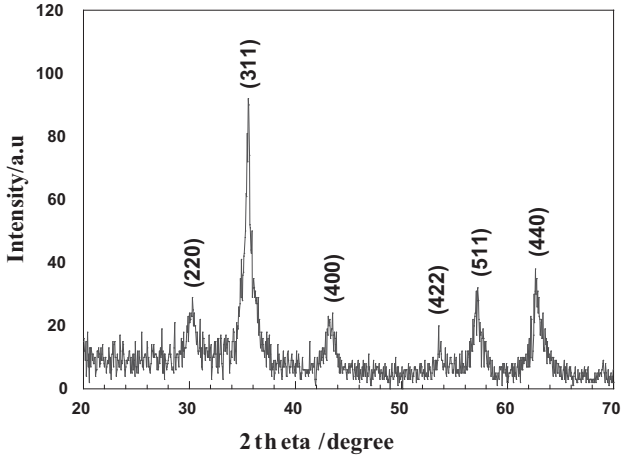

Figure 1 The powder X-ray diffraction pattern of the Fe_3O_4 NPs.

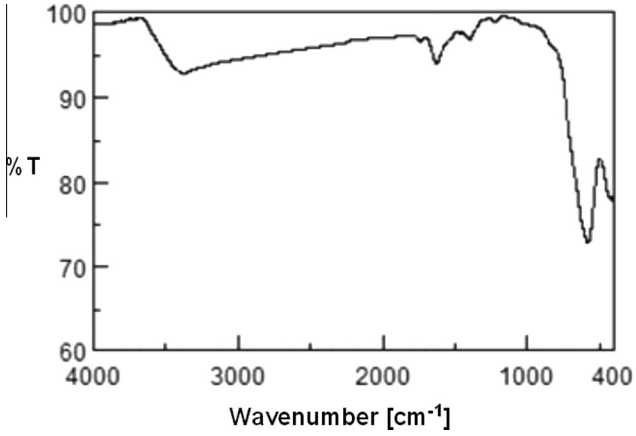

Figure 2 FT-IR spectra of Fe_3O_4 NPs.

Fig. 1. shows the powder X-ray diffraction (XRD) pattern for the Fe_3O_4 NPs. Although, the laboratory XRD diffractometers do not allow discriminating between the two possible cubic spinel phases of γ-Fe_2O_3 and magnetite (Fe_3O_4) due to their structural similarities (Cozzoli et al., 2006; Petkov et al., 2009; Buonsanti et al., 2010; Levy et al., 2011), our reaction conditions (Fe_3O_4 prepared under N_2 atmosphere) supplied Fe_3O_4 nanoparticles that were considered in literatures (Park et al., 2004). The γ-Fe_2O_3 particles could prepare at high temperature in air (Kang et al., 1996). A number of prominent Bragg reflections by their indices (220), (311), (400), (422), (511) and (440) reveal that the resultant magnetic NPs were Fe_3O_4 and structure is that of an inverse spinel (Park et al., 2004). The size of the magnetic NPs was also determined from X-ray line broadening by the use of Debye–Scherrer formula ($D = 0.9\lambda/\beta\cos\theta$, where D is the average crystalline size, λ is the X-ray wavelength used, β is the angular line width at half maximum intensity, and θ is the Bragg's angle). For the (311) reflection the average size of the Fe_3O_4 NPs was estimated to be around 11 nm.

The Fourier transform-infrared (FT-IR) spectrum of Fe_3O_4 NPs is shown in Fig. 2. The absorbance band at 583.3 cm^{-1} can be ascribed to Fe^{+2}–O^{-2}, which is consistent with the reported IR spectra for Fe_3O_4 NPs (Hoseini et al., 2013).

The morphology and microstructure of the NPs were further investigated by TEM analysis. Fig. 3A and B show TEM images that reveal spherical Fe_3O_4 NPs with an average size of 10–15 nm (Fig. 3C).

Fig. 4 shows the results for magnetization as a function of applied field at room temperature obtained for dry powder of Fe_3O_4 NPs. Magnetic measurement indicates magnetic behavior at room temperature for Fe_3O_4 NPs with no hysteresis behavior. For Fe_3O_4 NPs, the saturation magnetization value (Ms) is 57.8 emu/g while the reported value, Ms is 84 emu/g for the bulk Fe_3O_4 particles (Zhang and Wan, 2003). The measured magnetization of NPs was found to be considerably lower than the values measured from bulk magnetite.

Following our efforts to develop green methods in organic synthesis (Karami et al., 2013b,c; Khodabakhshi and Karami, 2012), we turned our attention toward the condensation of 4-hydroxycoumarin (**1**) and aryl glyoxals **2** in the presence of catalytic amounts of Iron oxide nanoparticles (Fe_3O_4 NPs) to produce dicoumarol derivatives **3** (Scheme 1).

To identify the suitable reaction conditions for the synthesis of **3** using Fe_3O_4 NPs, the reaction of 4-hydroxycoumarin (**1**) and phenyl glyoxal (**2a**) was selected as a model (Scheme 2).

As can be seen in Table 1, we found that in the absence of the catalyst, the reaction was not completed, even at long reaction times.

A higher loading of catalyst did not affect a marked influence on the product yield or reaction rate. Furthermore, in

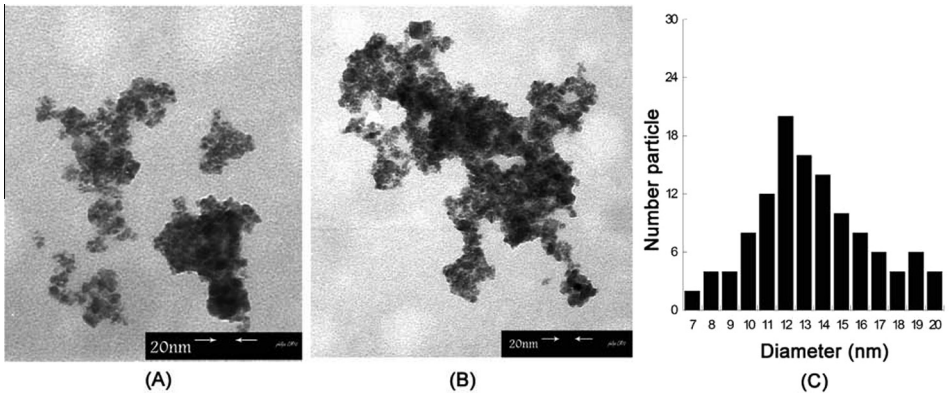

Figure 3 TEM images (A and B) show spherical Fe_3O_4 NPs with 10–15 nm and (C) the Histogram of particle size distribution.

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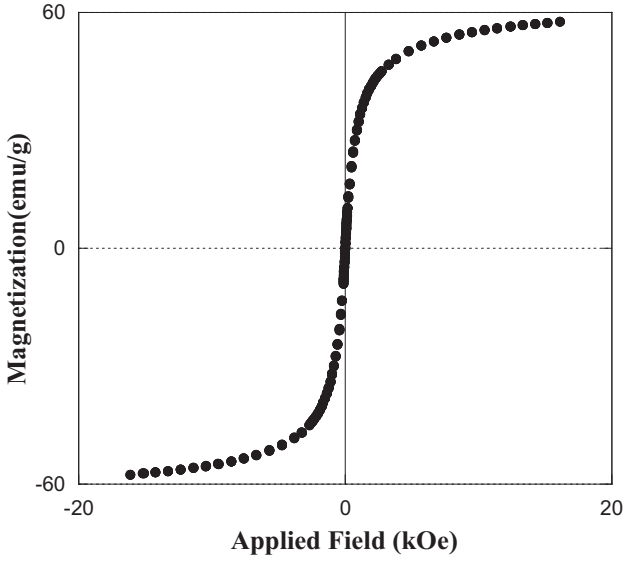
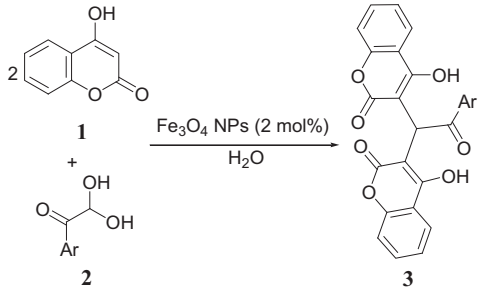
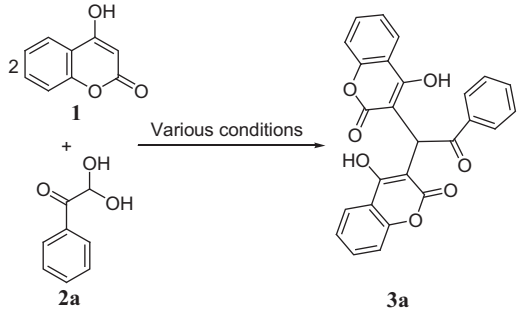


Figure 4 Room-temperature magnetization curve of magnetic Fe_3O_4 NPs.



Scheme 1 Synthesis of dicoumarol derivatives.



Scheme 2 Model reaction for optimization of conditions.

order to compare the Fe_3O_4 nanoparticles with bulk case, an experiment was also investigated. However, it was found that the model reaction proceeded slowly in the presence of Fe_3O_4 powder as bulk case (it needs 140 min to be completed).

In another experiment, in order to show the effect of solvent or media on the reaction progress, we employed several solvents for which the results have been shown in Table 2. It can be concluded that protonic solvents such as EtOH, MeOH, and H_2O can accelerate the condensation reaction.

It should be also noted that 4-hydroxycoumarin is soluble in alcohol, acetone and ether, but it has low solubility in water.

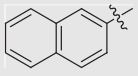
Table 1 Optimization of the reaction conditions in the synthesis of **3a** using several amounts of catalyst under reflux in H_2O.

Entry	Catalyst	Time (min)	Yield (%)
1	–	360	25
2	Fe_3O_4 NPs (1 mol%)	100	77
3	Fe_3O_4 NPs (2 mol%)	40	75
4	Fe_3O_4 NPs (5 mol%)	40	73
5	Fe_3O_4 powder (2 mol%)	70	65

Table 2 Effect of several solvents in synthesis of **3a** using Fe_3O_4 NPs (2 mol%) under reflux.

Entry	Solvent	Time (min)	Yield (%)
1	–	360	10
1	MeOH	40	77
2	EtOH	40	75
3	THF	45	73
4	CH_2Cl_2	360	50
5	EtOH/H_2O (1:1)	35	75
6	H_2O	40	75

Table 3 Synthesis of dicoumarols using Fe_3O_4 NPs (2 mol%) under reflux in H_2O.

Entry	Ar	Time (min)	Yield[a] (%)	Mp (°C)
3a	C_6H_5	40	75	177–175
3b	4-F-C_6H_4	35	73	273–235
3c	4-Br-C_6H_4	30	80	262–264
3d	4-NO_2-C_6H_4	30	86	270–272
3e	4-MeO-C_6H_4	35	75	265–267
3f	3-MeO-C_6H_4	40	70	205–207
3g	4-Cl-C_6H_4	45	75	250–252
3h		40	85	255–257

[a] Isolated yield.

Through screening, we found that this reaction was efficiently completed using Fe_3O_4 NPs (2 mol%) under reflux in H_2O about 40 min (entry 6). Subsequently, in order to prove the general applicability of this method, different aryl glyoxals were employed in the reaction with **1** (Table 3).

The nature of the Ar group showed no significant effect on the reaction rate or product yield. The use of water instead of organic solvents is more reasonable because of its safety and cheapness.

Mechanistically, the Scheme 3 shows a suggested mechanism to synthesize by Fe_3O_4. Making an active leaving group on aryl glyoxal by a Lewis acid such as iron (II, III) may be a reasonable start for the Knoevenagel condensation with 4-hydroxycoumarin (**1**). Subsequently, 1,4-addition of next 4-hydroxycoumarin to the formed α,β-unsaturated ketone can produce target molecule. This mechanism also shows the recyclability of Fe_3O_4 NPs.

Nano-magnetite (Fe_3O_4) as a support for recyclable catalysts in the development of sustainable methodologies has been

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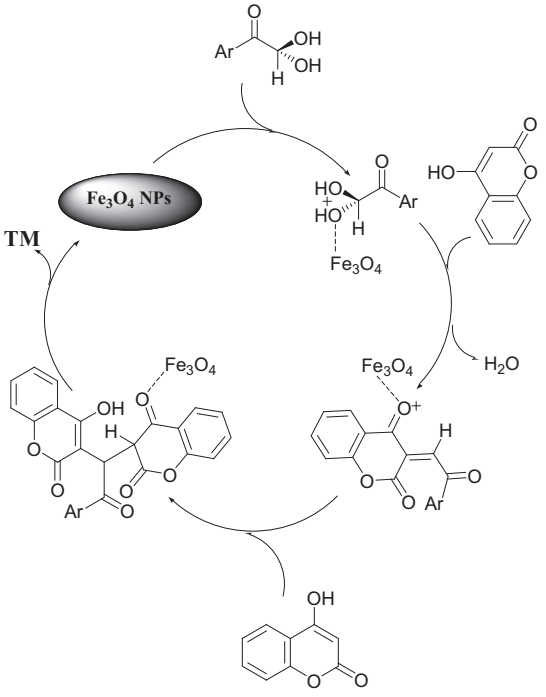

Scheme 3 Suggested mechanism for the synthesis of dicoumarol using Fe_3O_4 Nps.

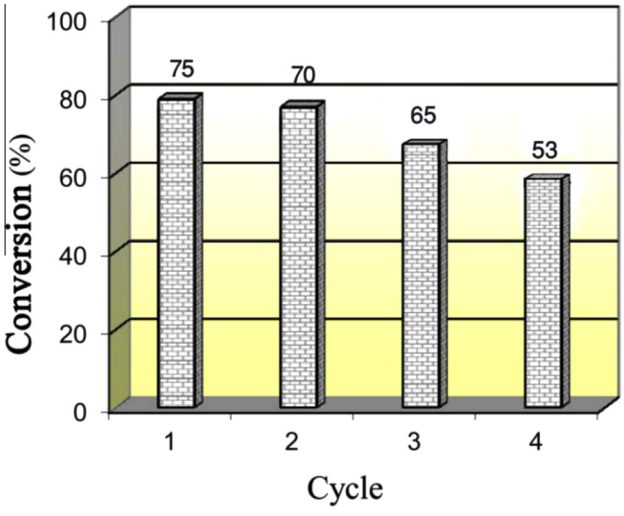

Figure 5 Recyclability of Fe_3O_4 NPs in synthesis of **3a**. Reaction time: 40 min.

recently reviewed by Gawande and co-workers (Gawande et al., 2013). To investigate the reusability of Fe_3O_4 NPs in the synthesis of dicoumarols **3**, this magnetically recyclable catalyst was reused 3 times (Fig. 5).

The results show that these magnetic nanoparticles are usable for 3 times without appreciable loss in catalytic activity and it is likely to be slowly aggregated after cycle 3 according to Fe_3O_4 NP aggregation in aqueous media (Butter et al., 2003). It should be noted that, here, we investigated the catalytic efficiency in a constant time (40 min) and the reaction was efficiently completed after 60 min for the cycle 4. Despite an observable decrease of catalytic activity in cycle 4, it is separable from the reaction mixture and reusable for the next step, but, acts like Fe_3O_4 powder. Totally, avoidance of organic solvents and use of separable catalysts are important factors in agreement with green chemistry principles.

4. Conclusions

In summary, we have described the preparation, characterization, and a new application of Fe_3O_4 nanoparticles as a magnetically recyclable catalyst in a condensation reaction to produce new dicoumarol containing an aroyl group. This reaction can be also regarded as a new approach for the preparation of pharmaceutically relevant heterocyclic systems. This method includes some important aspects such as use of environmentally friendly and recyclable catalyst, good productivity, short reaction times, and use of water as a clean media, which make this protocol in accord with green and sustainable chemistry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2014.05.030.

References

Ahmad, H., 2013. Magnetic polyaniline composites: recent developments in preparation, properties and applications. J. Colloid Sci. Biotechnol. 2, 155–170.

Barzegar, A., Davari, M.D., Chaparzadeh, N., Zarghami, N., Pedersen, J.Z., Incerpi, S., Saso, L., Moosavi-Movahedi, A.A., 2011. Theoretical and experimental studies on the structure-antioxidant activity relationship of synthetic 4-methylcoumarins. J. Iran. Chem. Soc. 8, 973–982.

Bellis, D.M., Spring, M.S., Stokerb, J.R., 1967. The biosynthesis of dicoumarol. Biochem. J. 103, 202–206.

Buonsanti, R., Grillo, V., Carlino, E., Giannini, C., Gozzo, F., Garcia-Hernandez, M., Garcia, M.A., Cingolani, R., Cozzoli, P.D., 2010. Architectural control of seeded-grown magnetic-semicondutor iron oxide-TiO(2) nanorod heterostructures: the role of seeds in topology selection. J. Am. Chem. Soc. 132, 2437–2464.

Butter, K., Bomans, P.H., Frederik, P.M., Vroege, G.J., Philipse, A.P., 2003. Direct observation of dipolar chains in ferrofluids in zero field using cryogenic electron microscopy. J. Phys.: Condens. Matter 15, S1451S1451.

Chanda, A., Fokin, V.V., 2009. Organic synthesis "on water". Chem. Rev. 109, 725–748.

Cherkupally, S.R., Mekala, R., 2008. Synthesis of novel 6,6′-methylene-bis-[3-(2-anilinoacetyl)-4-hydroxycoumarin] derivatives. Chem. Pharm. Bull. 56, 1732–1734.

Cozzoli, P.D., Snoeck, E., Garcia, M.A., Giannini, C., Guagliardi, A., Cervellino, A., Gozzo, F., Hernando, A., Achterhold, K., Ciobanu, N., Parak, F.G., Cingolani, R., Manna, L., 2006. Colloidal

synthesis and characterization of tetrapod-shaped magnetic nanocrystals. Nano Lett. 6, 1966–1972.

Fartani, M., Mangeney, C., Bousalem, S., Zhicai, M., Ammar, S., Herbst, F., Beaunier, P., Elaissari, A., Chehimi, M.M., 2007. Magnetic Fe_2O_3-polystyrene/PPy core/shell particles: bioreactivity and self-assembly. Langmuir 23, 10940–10949.

Gawande, M.B., Branco, P.S., Varma, R.S., 2013. Nano-magnetite (Fe_3O_4) as a support for recyclable catalysts in the development of sustainable methodologies. Chem. Soc. Rev. 42, 3371–3393.

Hamdi, N., Puerta, M.C., Valerga, P., 2008. Synthesis, structure, antimicrobial and antioxidant investigations of dicoumarol and related compounds. Eur. J. Med. Chem. 43, 2541–2548.

Hoseini, S.J., Nasrabadi, H., Azizi, M., Salimi-Beni, A., Khalifeh, R., 2013. Fe_3O_4 nanoparticles as an efficient and magnetically recoverable catalyst for Friedel–Crafts acylation reaction in solvent-free conditions. Synth. Commun. 43, 1683–1691.

Kang, Y.S., Risbud, S., Rabolt, J.F., Stroeve, P., 1996. Synthesis and characterization of nanometer-size Fe_3O_4 and γ-Fe_2O_3 particles. Chem. Mater. 8, 2209–2211.

Karami, B., Khodabakhshi, S., Nikrooz, M., 2011. Synthesis of azapolycyclic compounds: novel phenazines and quinoxalines using molybdate sulfuric acid (MSA). Polycycl. Aromat. Compd. 31, 97–109.

Karami, B., Khodabakhshi, S., Eskandari, K., 2012a. A one-pot, three-component synthesis of new pyrano[2,3-*h*]coumarin derivatives. Tetrahedron Lett. 53, 1445–1446.

Karami, B., Hoseini, S.J., Eskandari, K., Ghasemi, A., Nasrabadi, H., 2012b. Synthesis of xanthene derivatives by employing Fe_3O_4 nanoparticles as an effective and magnetically recoverable catalyst in water. Catal. Sci. Technol. 2, 331–338.

Karami, B., Hoseini, S.J., Nikoseresht, S., Khodabakhshi, S., 2012c. Fe_3O_4 nanoparticle: a powerful and magnetically recoverable catalyst for the synthesis of novel calix[4]resorcinarenes. Chin. Chem. Lett. 23, 173–176.

Karami, B., Nikoseresht, S., Khodabakhshi, S., 2012d. Novel approach to benzimidazoles using Fe_3O_4 nanoparticles as a magnetically recoverable catalyst. Chin. J. Catal. 33, 298–301.

Karami, B., Eskandari, K., Khodabakhshi, S., Hoseini, S.J., Hashemian, F., 2013a. Green synthesis of three substituted methane derivatives by employing ZnO nanoparticles as a powerful and recyclable catalyst. RSC Adv., 23335–23342.

Karami, B., Khodabakhshi, S., Hashemi, F., 2013b. Synthesis of a novel class of benzofurans via a three-component, regiospecific intramolecular heterocylization reaction. Tetrahedron Lett. 54, 3583–3585.

Karami, B., Jamshidi, M., Khodabakhshi, S., 2013c. Modified Paal–Knorr synthesis of novel and known pyrroles using tungstate sulfuric acid as a recyclable catalyst. Lett. Org. Chem. 10, 12–16.

Khodabakhshi, S., Karami, B., 2012. A rapid and eco-friendly synthesis of novel and known benzopyrazines using silica tungstic acid (STA) as a new and recyclable catalyst. Catal. Sci. Technol. 2, 1940–1944.

Kolos, N.N., Gozalishvili, L.L., Yaremenko, F.G., 2007. Aroyl[bis(4-hydroxycoumarin-3-yl)]methanes in reactions with 1,2-diaminobenzenes. Russ. Chem. Bull. 56, 2277–2283.

Levy, M., Quarta, A., Espinosa, A., Figuerola, A., Wilhelm, C., Garciia-Hernaáandez, M., Genovese, A., Falqui, A., Alloyeau, D., Buonsanti, R., Cozzoli, P.D., Garcia, M.A., Gazeau, F., Pellegrino, T., 2011. Correlating magneto-structural properties to hyperthermia performance of highly monodisperse iron oxide nanoparticles prepared by a seeded-growth route. Chem. Mater. 23, 4170–4180.

Link, K.P., 1941. Studies on hemorrhagic sweet clover disease: IV: the isolation and crystallization of the hemorrhagic agent. J. Biol. Chem. 138, 21–33.

Litinas, K.E., Mangos, A., Nikkou, T.E., Hadjipavlou-Litina, D.J., 2011. Synthesis and biological evaluation of fused oxepinocoumarins as free radicals scavengers. J. Enzyme Inhib. Med. Chem. 26, 805–812.

Liu, J.F., Zhao, Z.S., Jiang, G.B., 2008. Coating Fe_3O_4 magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. Environ. Sci. Technol. 42, 6949–6954.

Park, J., An, K., Hwang, Y., Park, J.G., Noh, H.J., Kim, J.Y., Park, J.H., Hwang, N.M., Hyeon, T., 2004. Ultra-large-scale syntheses of monodisperse nanocrystals. Nat. Mat. 3, 891–895.

Petkov, V., Cozzoli, P.D., Buonsanti, R., Cingolani, R., Ren, Y., 2009. Size, shape, and internal atomic ordering of nanocrystals by atomic pair distribution functions: a comparative study of γ-Fe_2O_3 nanosized spheres and tetrapods. J. Am. Chem. Soc. 131, 14264–14266.

Rahman, M.M., Ahmad, H., Islam, M.M., 2013. Preparation and potential applications of magnetically recyclable biocatalysts. J. Colloid Sci. Biotechnol. 2, 171–179.

Roveimiab, Z., Mahdavian, A.R., Biazar, E., Heidari, K.S., 2012. Preparation of magnetic chitosan nanocomposite particles and their susceptibility for cellular separation applications. J. Colloid Sci. Biotechnol. 1, 82–88.

Siddiqui, Z.N., Farooq, F., 2011. $Zn(Proline)_2$: a novel catalyst for the synthesis of dicoumarol. Catal. Sci. Technol. 1, 810–816.

Zhang, Z., Wan, M., 2003. Nanostructures of polyaniline composites containing nano-magnet. Synth. Met. 132, 205–212.

Ziarani, G.M., Hajiabbasi, P., 2013. Recent application of 4-hydroxycoumarin in multi-component reactions. Heterocycles 87, 1415–1439.

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